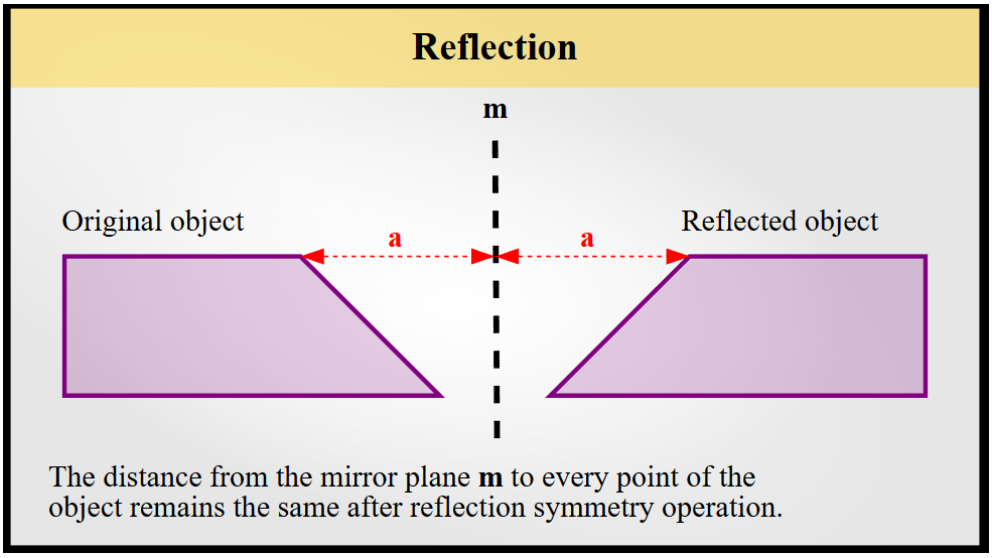
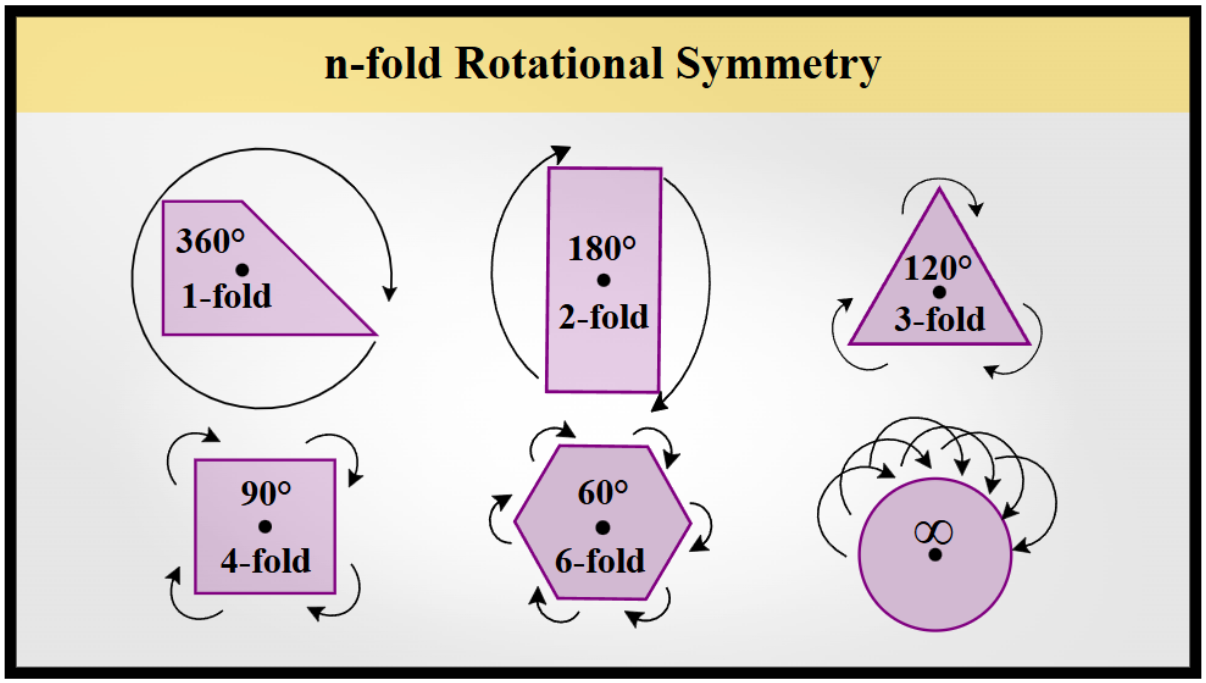
Symmetry Operations

1) **Reflection** is a symmetry operation which causes a set of points to be mirrored across a plane. We call this plane the "mirror plane." Any point (X,Y,Z) becomes (-X,Y,Z) if there is a mirror axis perpendicular to the X direction.

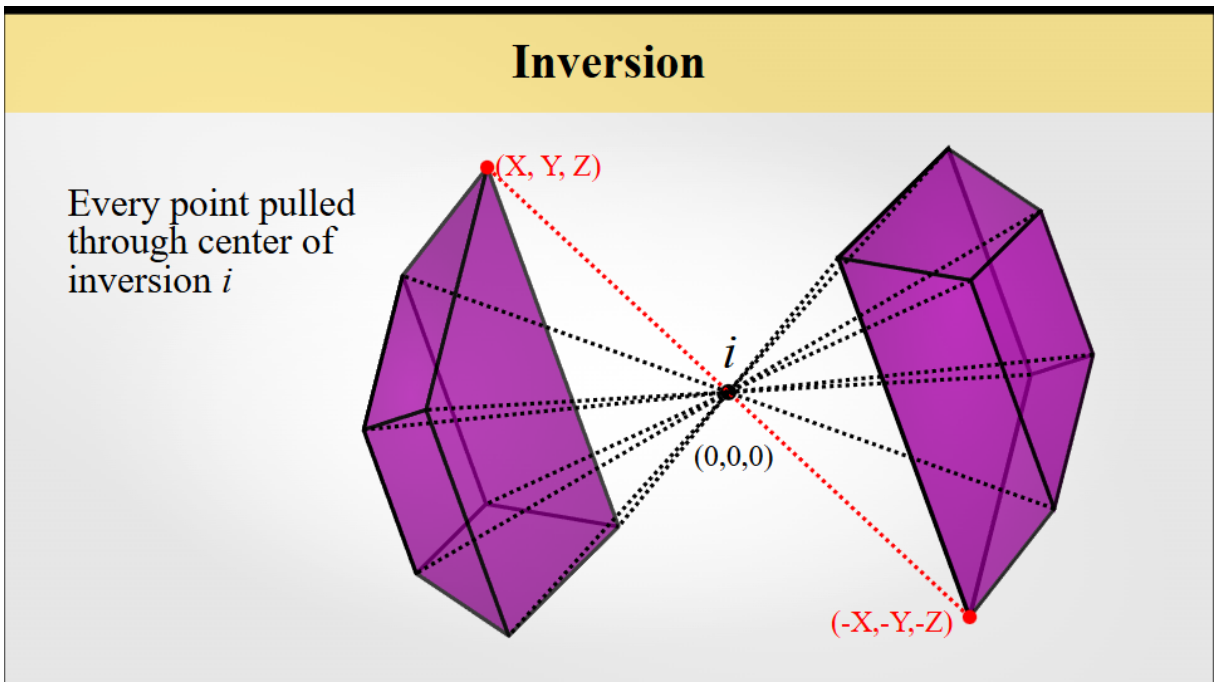


2) **Rotation** is a symmetry operation which causes a set of points to be rotated around a point. We call this point an "axis of rotation." In polar coordinates, any point (R, θ, ϕ) becomes (R, θ + 360º/n, ϕ) for an n- fold rotation axis perpendicular to θ.

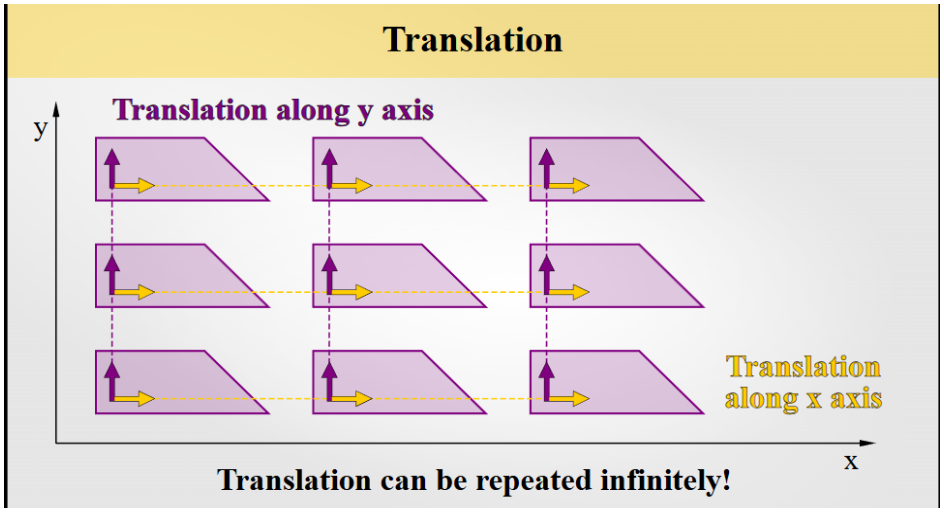
n	Angle
1	None
2	180
3	120
4	90
6	60



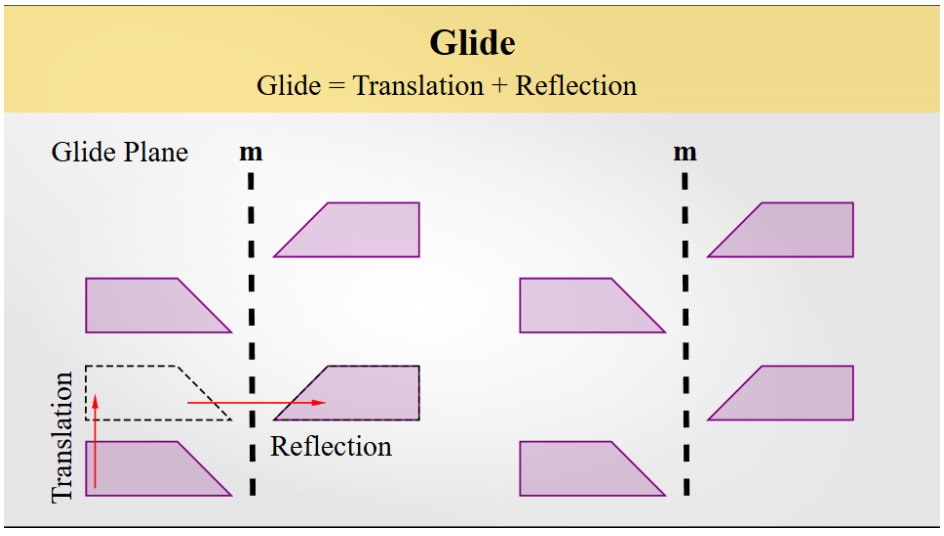
3) Inversion is a symmetry operation which pulls every point through an "inversion center" to the other side. Any point (X, Y, Z) becomes (-X, -Y, -Z) if there is an inversion center at the origin. You can combine rotation with inversion to produce the rotoinversion symmetry operation.



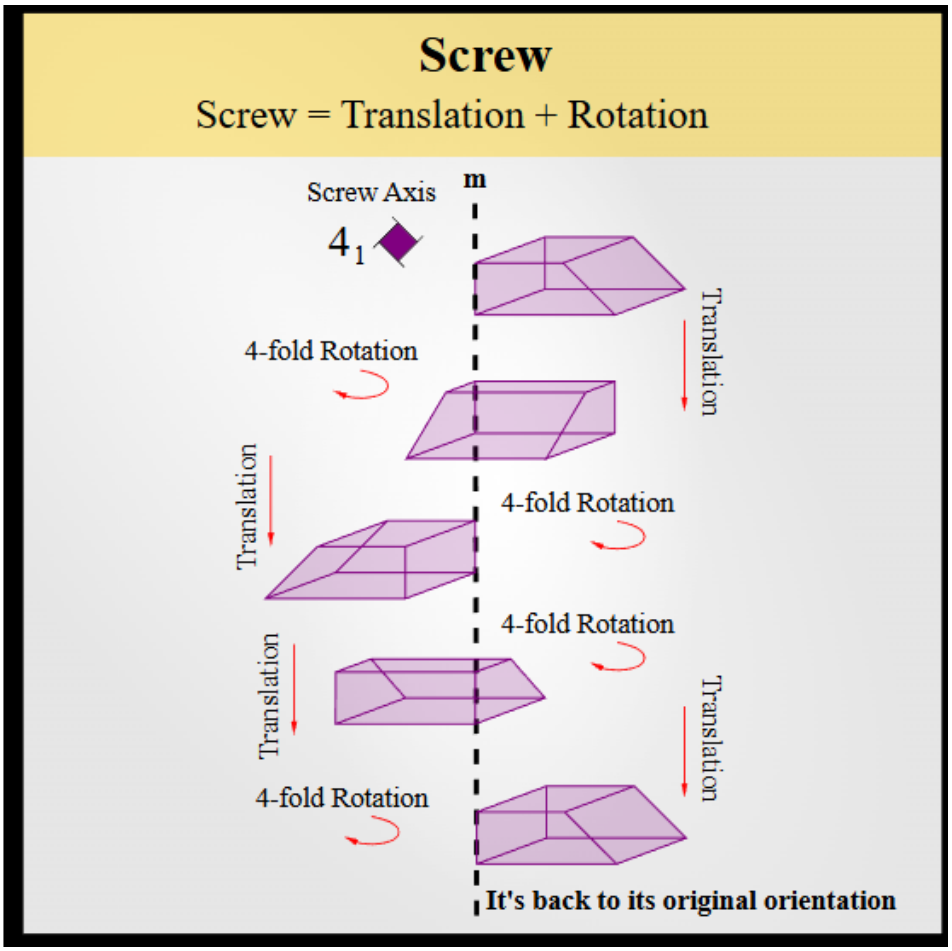
4) **Translation** is a symmetry operation that moves a set of points through space. Point groups DO NOT involve translation. Any point (X,Y,Z) becomes (X+a, Y, Z) for translation of length a in the X-direction.



5) **Glide** is a symmetry operation which combines translation + reflection. Objects are translated in the direction, and rotated across, the glide plane.



6) **Screw** is a symmetry operation which combines translation + rotation. Objects are translated down, and rotated around, the screw axis.



Point Groups

Introduction

A Point Group is a set of symmetry operations that leaves at least one point in space unchanged (hence "point" group).

They describe the external symmetry of a crystal or molecule but ignore translational symmetries.

Mathematically:

> A point group G is a finite subgroup of O(3) (orthogonal transformations in 3D) that preserves the lattice.

In crystallography:

- Only 32 crystallographic point groups exist (restrictions from periodicity).
- All 32 are expressed in Hermann–Mauguin (H–M) notation.

In DFT, point groups:

- Reduce k-point sampling
- Reduce number of irreducible atoms
- Reduce computational cost
- Define allowed tensor components (ε, σ, piezoelectric, elastic tensor)
- Determine magnetism (magnetic point groups)

H-M Symbol	Operation	Description
$\bar{1}$	Inversion	Inversion through the center.
$\bar{2}$	Rotate 180 + Invert	Equivalent to a Mirror Plane (m).
$\bar{3}$	Rotate 120 + Invert	present in trigonal groups
$\bar{4}$	Rotate 90 + Invert	Often implies a tetrahedron shape.
$\bar{6}$	Rotate 60 + Invert	Equivalent to a 3-fold axis + perpendicular mirror (3/m).

Combined Symbols

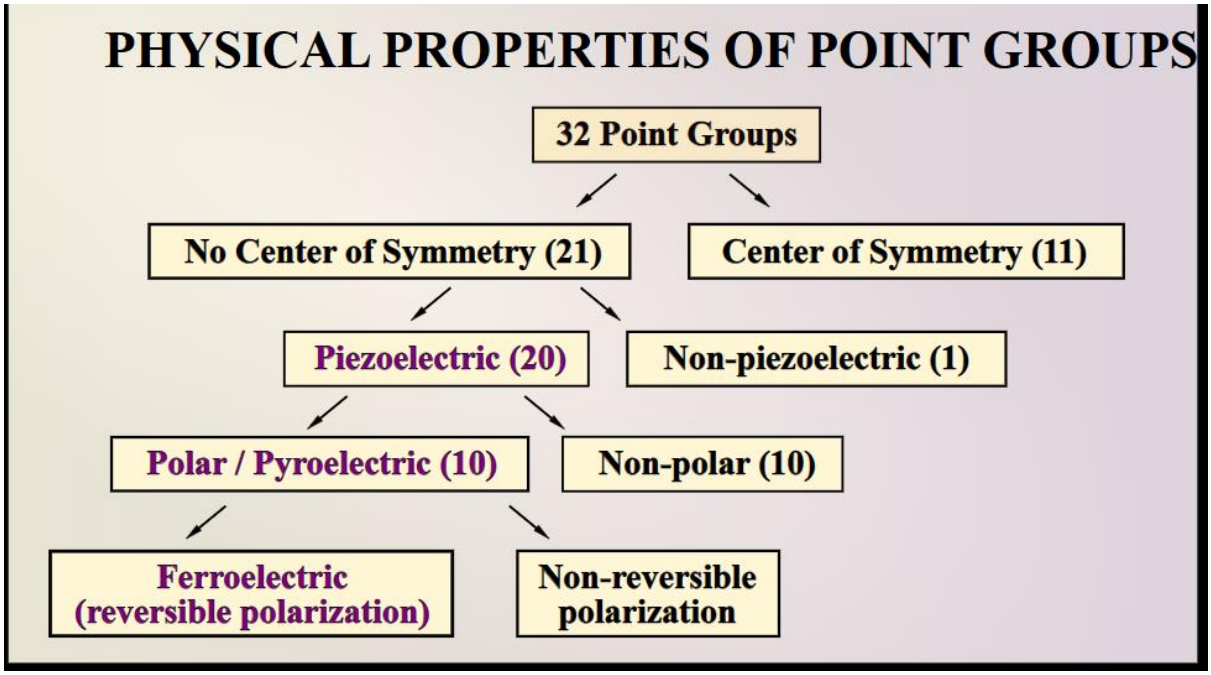
- mm = two perpendicular mirror planes
- mmm = three mutually perpendicular mirrors
- 4/mmm = rotation + horizontal mirror + vertical mirror set
- 6/m = rotation 6 + horizontal mirror
- m3 = cubic: mirrors + threefold axes

Table of 32 Point Groups

Crystal System	Point Groups (H–M)
Triclinic	1, −1
Monoclinic	2, m, 2/m
Orthorhombic	222, mm2, mmm
Tetragonal	4, 4/m , 433 , $\bar{4}$2m, 4/mmm
Trigonal	3, $\bar{3}$, 32, 3m, $\bar{3}$m
Hexagonal	6, $\bar{6}$, 6/m, 622, 6mm, $\bar{6}$m2, 6/mmm
Cubic	23, m3, 432, $\bar{4}$3m, m3m

Crystal symmetry is important because it can tell you certain potential properties about the material., Neumann's Principle says that if the crystal structure is identical along certain symmetries, then the crystal properties are also identical along those symmetries.

This can "forbid" certain properties which require asymmetry to exist.



- For example, piezoelectricity can only occur because of an asymmetry in the crystal cell, which allows the creation of an asymmetrical electric field. If the crystal structure has a center of symmetry, then piezoelectricity is completely impossible.

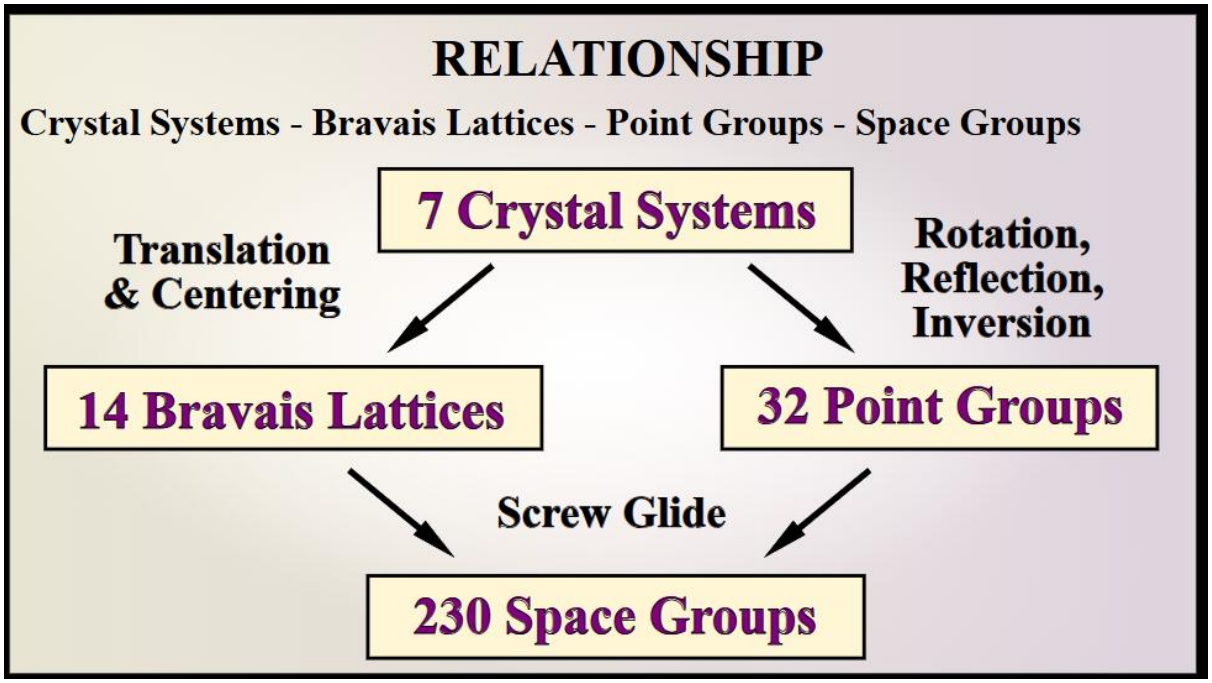
- Of the 32 point groups, 11 have a center of symmetry. Of the remaining 21 point groups, 20 can be piezoelectric (point group 432 can't be piezoelectric for other reasons).
- From this group of 20, 10 are polar, which means the cell can have an electric dipole and lead to "spontaneous electric polarization." Materials with this property are called pyroelectric.
- From the 10 pyroelectric point groups, all 10 have the potential to be ferroelectric, depending on the specifics of the crystal. Ferroelectric materials can have the pyroelectric spontaneous polarization reversed by an external field. Materials which are

pyroelectric, but not ferroelectric, cannot have the polarization reversed.

Property	Point Group
Center of Symmetry (11 Point Groups)	$\bar{1}$ $2/m$ mmm $4/m$ $\bar{3}$ $\bar{3}m$ $6/m$ $\bar{3}m$ $m\bar{3}m$ $4/mmm$ $6/mmm$
No Center of Symmetry (21 Point Groups)	23 432 $\bar{4}3m$ 6 $\bar{6}$ 622 $6mm$ $\bar{6}2m$ 3 32 $3m$ 4 $\bar{4}$ 422 $4mm$ $\bar{4}2m$ 222 $mm2$ 2 m 1
Piezoelectric (20 Point Groups)	23 $\bar{4}3m$ 6 $\bar{6}$ 622 $6mm$ $\bar{6}2m$ 3 32 $3m$ 4 $\bar{4}$ 422 $4mm$ $\bar{4}2m$ 222 $mm2$ 2 m 1
Pyroelectric (10 Point Groups)	6 $6mm$ 3 $3m$ 4 $4mm$ $mm2$ 2 m 1
Ferroelectric	All 10 point groups that are pyroelectric have the potential to be ferroelectric.

Space Groups

Space groups are mathematical constructs that capture every way an object can be repeated through space, through translation, rotation, reflection, screws, and gliding. In 3 dimensions, there are 230 space groups.



There are 230 space groups in 3-dimensions. In 2-dimensions, there are 17 plane groups (also called “wallpaper groups”). We can think of space groups as the combination of Bravais lattices and point groups.

- ## Space Group Notation

The international standard notation for space groups is shortened Hermann–Mauguin (H-M) notation. There is also a full H-M notation system which identifies all symmetry operations in each space group, but the shortened HM notation eliminates symmetry

operations which are not not necessary to uniquely identify a space group.

Space groups are also ordered by number.

In HM notation, the first letter is capitalized, and explains what kind of centering is present in the Bravais lattice. “P” stands for primitive, “C” stands for base-centered, “F” stands for face-centered, and “I” stands for body-centered.

After the centering letter, there are symmetry operations which operate on 3 different axes.

Positive numbers n means that there is n-fold rotation. Negative number n means there is n-fold rotoinversion. Numbers with a subscript XY indicated screw axes. The letter “m” stands for mirror planes. Any other lowercase letters refer to glide planes, such as “a,” “b,” “c,” “e” (glide along one face),”n” (glide along half diagonal of a face), and “d” (glide along ¼ diagonal of a face).

For example, space group 8 is C 1 m 1. The first letter is C, for base-centered. There is no symmetry in the first axis, a mirror plane in the 2nd axis, and nothing in the 3rd axis.

Another example, space group 47 is P 2/m 2/m 2/m. The P means there is no centering, and all 3 axes have both a 2-fold rotation and a mirror plane.

The same effect can be produced by combining multiple symmetry operations. This leads to abbreviated H-M notation, which omits some of these symmetry operations to the minimum which can uniquely identify a space group.

For example, going back to space group 8 and 47. C 1 m 1 just becomes Cm, because the 1s are not telling you anything special. P 2/m 2/m 2/m becomes Pmmm, because 3 mirror planes must be perpendicular to each other, which automatically creates a 2-fold rotation in each axis.